

## PATENT COOPERATION TREATY

PCT

## NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents  
United States Patent and Trademark  
Office  
Box PCT  
Washington, D.C. 20231  
ÉTATS-UNIS D'AMÉRIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 14 January 2000 (14.01.00)	
International application No. PCT/FI99/00359	Applicant's or agent's file reference VUO2PCT
International filing date (day/month/year) 30 April 1999 (30.04.99)	Priority date (day/month/year) 30 April 1998 (30.04.98)
Applicant VUORINEN, Tapani	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:  
22 November 1999 (22.11.99)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was  
☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

<p>The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland</p> <p>Facsimile No.: (41-22) 740.14.35</p>	<p>Authorized officer A. Karkachi</p> <p>Telephone No.: (41-22) 338.83.38</p>
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## TENT COOPERATION TREE

PCT

NOTIFICATION OF THE RECORDING  
OF A CHANGE(PCT Rule 92bis.1 and  
Administrative Instructions, Section 422)

From the INTERNATIONAL BUREAU

To:

SEPPO LAINE OY  
Itämerenkatu 3 B  
FIN-00180 Helsinki  
FINLANDE

<b>Date of mailing</b> (day/month/year) 22 March 2000 (22.03.00)	<b>IMPORTANT NOTIFICATION</b>
<b>Applicant's or agent's file reference</b> VUO2PCT	
<b>International application No.</b> PCT/FI99/00359	<b>International filing date</b> (day/month/year) 30 April 1999 (30.04.99)

1. The following indications appeared on record concerning:		
<input checked="" type="checkbox"/> the applicant	<input type="checkbox"/> the inventor	<input type="checkbox"/> the agent <input type="checkbox"/> the common representative
Name and Address	State of Nationality	State of Residence
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	
2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:		
<input type="checkbox"/> the person	<input type="checkbox"/> the name	<input type="checkbox"/> the address <input type="checkbox"/> the nationality <input type="checkbox"/> the residence
Name and Address METSÄ-SERLA OYJ Revontulentie 6 FIN-02100 Espoo Finland	State of Nationality FI	State of Residence FI
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	
3. Further observations, if necessary: <b>New applicant for the purposes of all designated States except US. The status of VUORINEN, Tapani has been changed to applicant/inventor for US only.</b>		
4. A copy of this notification has been sent to:		
<input checked="" type="checkbox"/> the receiving Office	<input type="checkbox"/> the designated Offices concerned	
<input type="checkbox"/> the International Searching Authority	<input checked="" type="checkbox"/> the elected Offices concerned	
<input checked="" type="checkbox"/> the International Preliminary Examining Authority	<input type="checkbox"/> other:	

<b>The International Bureau of WIPO</b> 34, chemin des Colombettes 1211 Geneva 20, Switzerland	<b>Authorized officer</b>  Aino Metcalfe
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38

The demand must be filed directly with the competent International Preliminary Examining Authority or, if two or more Authorities are competent, with the one chosen by the applicant. The full name or two-letter code of that Authority may be indicated by the applicant on the line below:

IPEA/ SE

# PCT

## CHAPTER II

### DEMAND

under Article 31 of the Patent Cooperation Treaty:  
The undersigned requests that the international application specified below be the subject of international preliminary examination according to the Patent Cooperation Treaty and hereby elects all eligible States (except where otherwise indicated).

For International Preliminary Examining Authority use only		
Identification of IPEA		Date of receipt of DEMAND
<b>Box No. I IDENTIFICATION OF THE INTERNATIONAL APPLICATION</b>		Applicant's or agent's file reference <b>VUO 2 PCT</b>
International application No. <b>PCT/FI99/ 00359</b>	International filing date (day/month/year) <b>30 April 1999 (30.04.99)</b>	(Earliest) Priority date (day/month/year) <b>30 April 1998 (30.04.98)</b>
Title of invention <b>A method of producing a fiber product</b>		
<b>Box No. II APPLICANT(S)</b>		
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)  <b>VUORINEN, Tapani Väli-Henttaantie 14 B FIN-02200 Espoo Finland</b>		Telephone No.:  Facsimile No.:  Teleprinter No.:
State (that is, country) of nationality: <b>Finland</b>	State (that is, country) of residence: <b>Finland</b>	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)		
State (that is, country) of nationality:	State (that is, country) of residence:	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)		
State (that is, country) of nationality:	State (that is, country) of residence:	
<input type="checkbox"/> Further applicants are indicated on a continuation sheet.		

**Box No. III AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE**The following person is ☒ agent ☐ common representativeand ☒ has been appointed earlier and represents the applicant(s) also for international preliminary examination.☐ is hereby appointed and any earlier appointment of (an) agent(s)/common representative is hereby revoked.☐ is hereby appointed, specifically for the procedure before the International Preliminary Examining Authority, in addition to the agent(s)/common representative appointed earlier.Name and address: *(Family name followed by given name; for a legal entity, full official designation.  
The address must include postal code and name of country.)*SEPPÖ LAINE OY  
Itämerenkatu 3 B  
FIN-00180 Helsinki  
Finland

Telephone No.:

+358-9-68 59 560

Facsimile No.:

+358-9-68 59 56 10

Teleprinter No.:

☐ Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.**Box No. IV BASIS FOR INTERNATIONAL PRELIMINARY EXAMINATION****Statement concerning amendments:\***

1. The applicant wishes the international preliminary examination to start on the basis of:

☒ the international application as originally filed

the description

☐ as originally filed☐ as amended under Article 34

the claims

☐ as originally filed☐ as amended under Article 19 (together with any accompanying statement)☐ as amended under Article 34

the drawings

☐ as originally filed☐ as amended under Article 342. ☐ The applicant wishes any amendment to the claims under Article 19 to be considered as reversed.3. ☐ The applicant wishes the start of the international preliminary examination to be postponed until the expiration of 20 months from the priority date unless the International Preliminary Examining Authority receives a copy of any amendments made under Article 19 or a notice from the applicant that he does not wish to make such amendments (Rule 69.1(d)). *(This check-box may be marked only where the time limit under Article 19 has not yet expired.)*

\* Where no check-box is marked, international preliminary examination will start on the basis of the international application as originally filed or, where a copy of amendments to the claims under Article 19 and/or amendments of the international application under Article 34 are received by the International Preliminary Examining Authority before it has begun to draw up a written opinion or the international preliminary examination report, as so amended.

Language for the purposes of international preliminary examination: English☐ which is the language in which the international application was filed.☐ which is the language of a translation furnished for the purposes of international search.☒ which is the language of publication of the international application.☐ which is the language of the translation (to be) furnished for the purposes of international preliminary examination.**Box No. V ELECTION OF STATES**The applicant hereby elects all eligible States *(that is, all States which have been designated and which are bound by Chapter II of the PCT)*

excluding the following States which the applicant wishes not to elect:

**Box No. VI CHECK LIST**

The demand is accompanied by the following elements, in the language referred to in Box No. IV, for the purposes of international preliminary examination:

- |  |   |        |
|--|---|--------|
| 1. translation of international application                              | : | sheets |
| 2. amendments under Article 34   | : | sheets |
| 3. copy (or, where required, translation) of amendments under Article 19 | : | sheets |
| 4. copy (or, where required, translation) of statement under Article 19  | : | sheets |
| 5. letter  | : | sheets |
| 6. other (specify)   | : | sheets |

For International Preliminary Examining Authority use only

received	not received
<input type="checkbox"/>	<input type="checkbox"/>
<input type="checkbox"/>	<input type="checkbox"/>
<input type="checkbox"/>	<input type="checkbox"/>
<input type="checkbox"/>	<input type="checkbox"/>
<input type="checkbox"/>	<input type="checkbox"/>
<input type="checkbox"/>	<input type="checkbox"/>

The demand is also accompanied by the item(s) marked below:

- |  |   |
|--|---|
| 1. <input checked="" type="checkbox"/> fee calculation sheet                             | 4. <input type="checkbox"/> statement explaining lack of signature                                  |
| 2. <input type="checkbox"/> separate signed power of attorney                            | 5. <input type="checkbox"/> nucleotide and or amino acid sequence listing in computer readable form |
| 3. <input type="checkbox"/> copy of general power of attorney; reference number, if any: | 6. <input type="checkbox"/> other (specify):  |

**Box No. VII SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE**

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the demand).

For the Applicants

Seppo Laine Oy

Christoffer Sundman

**For International Preliminary Examining Authority use only**

1. Date of actual receipt of DEMAND:

2. Adjusted date of receipt of demand due to CORRECTIONS under Rule 60.1(b):

3. ☐ The date of receipt of the demand is AFTER the expiration of 19 months from the priority date and item 4 or 5, below, does not apply.

☐ The applicant has been informed accordingly.

4. ☐ The date of receipt of the demand is WITHIN the period of 19 months from the priority date as extended by virtue of Rule 80.5.

5. ☐ Although the date of receipt of the demand is after the expiration of 19 months from the priority date, the delay in arrival is EXCUSED pursuant to Rule 82.

**For International Bureau use only**

Demand received from IPEA on:

## TENT COOPERATION TREA

PCT

From the INTERNATIONAL BUREAU

NOTIFICATION OF THE RECORDING  
OF A CHANGE(PCT Rule 92bis.1 and  
Administrative Instructions, Section 422)

To:

SEPPO LAINE OY  
Itämerenkatu 3 B  
FIN-00180 Helsinki  
FINLANDE

Date of mailing (day/month/year)

22 March 2000 (22.03.00)

Applicant's or agent's file reference

VUO2PCT

## IMPORTANT NOTIFICATION

International application No.

PCT/FI99/00359

International filing date (day/month/year)

30 April 1999 (30.04.99)

## 1. The following indications appeared on record concerning:

☒ the applicant ☐ the inventor ☐ the agent ☐ the common representative

Name and Address

State of Nationality

State of Residence

Telephone No.

Facsimile No.

Teleprinter No.

## 2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☐ the person ☐ the name ☐ the address ☐ the nationality ☐ the residence

Name and Address

METSÄ-SERLA OYJ  
Revontulentie 6  
FIN-02100 Espoo  
Finland

State of Nationality

FI

State of Residence

FI

Telephone No.

Facsimile No.

Teleprinter No.

## 3. Further observations, if necessary:

**New applicant for the purposes of all designated States except US. The status of VUORINEN, Tapani has been changed to applicant/inventor for US only.**

## 4. A copy of this notification has been sent to:

☒ the receiving Office ☐ the designated Offices concerned  
☐ the International Searching Authority ☒ the elected Offices concerned  
☒ the International Preliminary Examining Authority ☐ other:The International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer

Aino Metcalfe

Telephone No.: (41-22) 338.83.38

REC'D 23 AUG 2000

WIPO

PCT

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

16

Applicant's or agent's file reference VUO 2 PCT	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/FI99/00359	International filing date (day/month/year) 30.04.1999	Priority date (day/month/year) 30.04.1998
International Patent Classification (IPC) or national classification and IPC <sub>7</sub> D 21 H 17/25		
Applicant Metsä-Serla OYJ et al		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 4 sheets, including this cover sheet.
- ☒ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 3 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand  22.11.1999	Date of completion of this report  11.08.2000
Name and mailing address of the IPEA/SE Patent- och registreringsverket Box 5055 S-102 42 STOCKHOLM Facsimile No. 08-667 72 88	Authorized officer  Barbro Nilsson/mj Telephone No. 08-782 25 00

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/FI99/00359

## I. Basis of the report

1. This report has been drawn on the basis of *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.)*:

- ☐ the international application as originally filed.
- ☒ the description, pages 1-16, as originally filed,  
 pages \_\_\_\_\_, filed with the demand,  
 pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_,  
 pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_.
- ☒ the claims, Nos. \_\_\_\_\_, as originally filed,  
 Nos. \_\_\_\_\_, as amended under Article 19,  
 Nos. \_\_\_\_\_, filed with the demand,  
 Nos. 1-21, filed with the letter of 05.06.2000,  
 Nos. \_\_\_\_\_, filed with the letter of \_\_\_\_\_.
- ☒ the drawings, sheets/fig 1-7, as originally filed,  
 sheets/fig \_\_\_\_\_, filed with the demand  
 sheets/fig \_\_\_\_\_, filed with the letter of \_\_\_\_\_,  
 sheets/fig \_\_\_\_\_, filed with the letter of \_\_\_\_\_.

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages \_\_\_\_\_
- ☐ the claims, Nos. \_\_\_\_\_
- ☐ the drawings, sheets/fig \_\_\_\_\_

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the supplemental Box (Rule 70.2(c)).

4. Additional observations, if necessary:



## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/FI99/00359

**V. Resoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement****1. Statement**

Novelty (N)	Claims	<u>1-21</u>	YES
	Claims		NO
Inventive step (IS)	Claims	<u>1-21</u>	YES
	Claims		NO
Industrial applicability (IA)	Claims	<u>1-21</u>	YES
	Claims		NO

**2. Citations and explanations**

The claimed invention relates to a method of producing a modified fibre product of cellulosic material and to the modified fibre product.

In the invention an alkyl derivative of cellulose, in at least a partly water-soluble form, is mixed into a fibre suspension with alkali conditions and the subsequent derivative is bonded into the fibrous material prior to drying. A web produced of this material has good strength properties and a high water absorption capability.

Amended claims have been filed with the letter of 5 June 2000. Claim 1 now incorporates that "the alkyl derivatives of cellulose are mainly alkali-soluble." The dependent claims 9 and 21 have been adapted to the new claim 1 and the lower end value of the DP range has been changed from 100 to 600.

The most relevant prior art cited in the International Search Report:

D1 US 5354424 A  
D2 WO 9633310 A1  
D3 EP 0273075 A1

In document D1 a paper is treated with a cellulose derivative e.g. carboxymethyl cellulose (CMC) to increase the strength of the paper. The description discloses that the cellulose derivative can also be incorporated into paper furnish, column 6, lines 56-57 and example 7-8. D2 discloses the use of CMC in a composition added to papermaking furnish as a crepe facilitating agent. In D3 the use of CMC in a paper sheet for water-absorbency material is disclosed.

.../...

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/FI99/00359

**Supplemental Box**

(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: V.

The subject matter claimed differs from the product and method in D1 in that the cellulose derivative is soluble in mainly alkaline conditions. There is no indication in D1 to this aspect. The alkaline condition gives such a well bond that it cannot be washed away while derivatives of small molecular size such as those used in the D1 are water soluble and as a result they are easily washed away.

Documents D2 and D3 show the use of CMC in papermaking. However, there is no teaching towards the present invention.

According to the arguments above, the claimed invention is novel, is considered to involve an inventive step and to have industrial applicability.

**Claims:**

1. A method of producing a modified fiber product, according to which method

- cellulosic raw material is formed into a fiber suspension,
- 5 - components modifying the properties of fibers are added to the fiber suspension  
and
- the fiber material is dried,

**characterized in that**

- an alkyl derivative of cellulose, which is water-soluble in mainly alkaline  
10 conditions, is mixed into the fiber suspension in alkaline conditions, the derivative  
being at least partly dissolved in water, and
- the derivative is allowed to be bonded to the fibrous raw material prior to drying  
the fibrous material so that the bonded cellulose derivative can not be washed off  
with water.

15

2. A method according to claim 1, **characterized** in that a paper or paperboard web having  
good strength properties or good water retention is produced.

3. A method according to claim 1, **characterized** in that a cellulose product having good  
20 water retention is produced for use in hygiene products.

4. A method according to any of claims 1 - 3, **characterized** in that the used alkyl  
derivative of cellulose is carboxymethyl cellulose, carboxyethyl cellulose, methyl  
cellulose, ethyl cellulose or ether derivatives of any of these.

25

5. A method according to any of the previous claims, **characterized** in that the alkyl  
derivative of cellulose is allowed to be sorbed to the cellulose from the water phase so that  
at least 10 %, preferably 20 %, and especially preferably at least 30 % of the derivative  
contained by the water phase is allowed to be sorbed to the cellulose.

30

6. A method according to any of the previous claims, **characterized** in that the pH value of  
the pulp is more than 8, preferably more than 10.

05 -06- 2000

7. A method according to any of the previous claims, **characterized** in that the pulp is mixed with the cellulose derivative for at least 5 minutes, preferably at least 10 minutes and especially preferably for at least 20 minutes before drying.
- 5 8. A method according to any of claims 1 - 7, **characterized** in that the cellulose derivative to be sorbed is alkali soluble carboxymethyl cellulose (CMC), the DS of which being less than 0.5.
9. A method according to claim 8, **characterized** in that the polymerization degree of the  
10 CMC is about 600 - 5000.
10. A method according to claim 8 or 9, **characterized** in that the DS of the CMC is 0.2 - 0.4.
- 15 11. A method according to any of claims 1 - 7, **characterized** in that the cellulose derivative to be sorbed is hydroxy-propyl-methyl cellulose (HPMC), hydroxy-ethyl-methyl cellulose (HEMC) and hydroxy-buthyl-methyl cellulose (HBMC).
12. A method according to any of the previous claims, **characterized** in that about 10 %, at  
20 the most, of the cellulose derivative can be washed off the treated fibrous raw material at a temperature of 25 °C and a neutral pH value.
13. A method according to any of the previous claims, **characterized** in that in comparison with untreated paper, the same internal bond strength is achieved while using at least 10 %  
25 less pulp.
14. A method according to any of the previous claims, **characterized** in that the cellulose derivative is contacted with the cellulose fibers in an alkaline flow of a pulp or paper mill.
- 30 15. A method according to claim 14, **characterized** in that the cellulose derivative is contacted with the cellulose fibers in an alkaline bleaching stage, such as an oxygen (O) or peroxide (P) stage.

16. A method according to claim 15, **characterized** in that the cellulose derivative is contacted with the cellulose fibers in the peroxide bleaching of mechanical pulp.
17. A method according to claim 16, **characterized** in that the cellulose derivative is first  
5 contacted with chemical pulp, subsequent to which the pulp is drained and the filtrate is introduced to the peroxide bleaching of mechanical pulp.
18. A method according to claim 14, **characterized** in that the cellulose derivative is mixed with the cellulose fibers subsequent to the beating of fibers.
- 10 19. A method according to any of the previous claims, **characterized** in that the web forming is performed without an intermediate drying of pulp after sorption of the cellulose derivative.
- 15 20. A method according to any of the previous claims, **characterized** in that the amount of cellulose derivative is 0.1 to 5 % by weight of the cellulose fibers.
21. A modified fiber product, **characterized** in that it contains at least 0.1 % of CMC by (dry) weight of the fibers bonded to the fibers, the DP of the CMC being about 600 - 5000  
20 and the DS about 0.1 - 0.4.

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>D21H 17/25</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 99/57370</b> <b>(43) International Publication Date:</b> 11 November 1999 (11.11.99)
<b>(21) International Application Number:</b> PCT/FI99/00359 <b>(22) International Filing Date:</b> 30 April 1999 (30.04.99)  <b>(30) Priority Data:</b> 980968 30 April 1998 (30.04.98) FI  <b>(71)(72) Applicant and Inventor:</b> VUORINEN, Tapani [FI/FI]; Väli-Henttaantie 14 B, FIN-02200 Espoo (FI).  <b>(74) Agent:</b> SEPPO LAINE OY; Itämerenkatu 3 B, FIN-00180 Helsinki (FI).		<b>(81) Designated States:</b> AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> <i>In English translation (filed in Finnish).</i>
<b>(54) Title:</b> A METHOD OF PRODUCING A FIBER PRODUCT		
<b>(57) Abstract</b>  The present invention relates to a modified fiber product and a method of producing same. According to the method, the cellulosic raw material is formed into a fiber suspension, into which components modifying the properties of the fibers are added, subsequent to which the fibrous material is dried in connection with, for example, web forming. According to the invention, alkyl derivative of cellulose is mixed into the fiber suspension in alkaline conditions, the derivative being at least partly dissolved in water, and the derivative is allowed to be sorbed into the fibrous material prior to drying such that the sorbed cellulose derivative can not be washed off with water. The strength properties or the water retention of paper and paperboard products can be improved by using the invention.		

**FOR THE PURPOSES OF INFORMATION ONLY**

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DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

## A method of producing a fiber product

The present invention relates to a method according to the preamble of claim 1 for  
5 producing a fiber product. According to the method, a cellulosic raw material is formed into a fiber suspension, into which components modifying the properties of the fibers are introduced, subsequent to which the suspension is dried.

The invention is especially related to a method of producing a web having good strength  
10 properties and a high water absorption capability.

The invention also relates to a fiber product as described in the preamble of claim 21.

It is known in prior art that the properties of the cellulose fibers used for producing paper  
15 can be modified by adding polymers to the fiber suspension (pulp) prior to wire forming. Suitable additive materials include starch-based components, such as cationed starch, and different kinds of plastic materials, such as polyacryl polymers and polyamineamide-, polyamine- and acrylamino-epichlorohydrine polymers. Conventionally, the amounts added are about 0.5 - 5 % (by weight) of the pulp dry material.

20

The above-mentioned polymers can be used for increasing the dry and wet strength and water absorption of papers. A drawback of the known methods is, however, the relatively weak bonding between the conventional polymers and the cellulose fibers. For this reason the materials accumulate in the water circulation of the paper machine, which causes  
25 additional problems in treating and cleaning white water. Another drawback of the synthetic materials is their bad biodegradability, which affects the recycling and composting of the paper manufactured from the pulp.

Anionic polymers containing carboxyl groups or carboxylate ions in the form of alkali  
30 metals or ammonium salts are often added to the pulp to improve the retention of the cationic polymers. Carboxyalkylated polysaccharides, such as carboxymethyl cellulose, CMC (see for example US patents 5,061,346 and 5,316,623) can especially be mentioned as examples of anionic polymers. Usually, these polymers are added to the pulp in larger



quantities than the usual modifying chemicals, i.e. the amount is typically about 5 - 20 % of the fiber material content of the pulp.

A drawback of the mixing of cationic and anionic polymers is that they might react  
5 together and macrocoagulate, if they are added together or if the anionic polymer is introduced to the fibers before the cationic modifying chemicals. For this reason it is difficult to evenly distribute the cation polymer in the fibers. Additionally, using several different components will further affect the treatment of white water.

10 There are also prior art solutions, in which the strength properties of papers are enhanced by adding mainly only alkyl derivatives of cellulose as modifying agents. The GB patent publication 978 953 describes a method of forming a fiber web having good strength properties, according to which method a hydrophilic bonding compound is produced from cellulose ether, which is then mixed with the pulp or water phase either in swollen form or  
15 as a gel. The amount of bonding compound added to the pulp can be as high as 25 % of the amount of pulp. According to the above patent publication, the method produces very even sheets, and the bonding compound increases the bonds between the fibers, thus increasing the strength of the sheet.

20 However, the solution is a complex one and difficult to apply on an industrial scale, because the cellulose ether will first have to be extruded for forming a bonding compound having a suitable composition.

US patent publication 5,275,698 describes a method of adding cellulose polymers to the  
25 pulp. The cloud point of the utilized cellulose polymers is between 10 - 95 °C, and their solubility is inversely proportional to the temperature. When the polymer is added as water solution to the pulp in a temperature below the cloud point, the temperature of the pulp being higher than the cloud point of the polymer, the polymer is caused to coagulate into a colloid as it is dispersed into the pulp.

30

In the method according to the US patent publication the coagulation of the polymers is difficult to control, and during introduction the pulp must be vigorously agitated in order to uniformly distribute the polymer into the fibers.

The present invention relates to a method of removing the drawbacks associated with the prior art and to achieve a totally novel solution for modifying the properties of cellulose fibers. The invention especially relates to a method of bonding the cellulose derivative, especially a derivative of alkylated cellulose, such as carboxymethyl cellulose, to the fibers of the cellulose pulp even without any retention enhancers so that the cellulose derivative can not be washed off.

The present invention is based on the idea that an alkyl derivative of cellulose in at least partially water-soluble form is added to the pulp in alkali conditions, and that the derivative is allowed to bond into the fibrous raw material prior to drying in connection with e.g. web forming. The bonding (sorption) is secured by allowing the cellulose derivative to contact the cellulose for a sufficient period of time.

When using CMC as the cellulose derivative, the modified fiber product according to the invention will contain at least 0.1 % of bonded CMC by (dry) weight of the fibers, the DP of which is about 100 - 5000 and DS about 0.1 - 0.4.

More specifically, the method according to the invention is mainly characterized by what is stated in the characterizing part of claim 1.

The the fiber product according to the invention, on the other hand, is characterized by what is stated in the characterizing part of claim 21.

The solution according to the invention will accomplish considerable advantages. Thus, the strength properties of paper manufactured from cellulose pulp according to the invention can be considerably increased. Increase of internal bond strength (the density of the sheet remains constant) shows an increase of specific bond strength. Tensile strength and stretch at break are accordingly increased. Therefore, pulps produced according to the invention can be used in all applications, in which the strength of paper is of importance. Sorption of cellulose derivative, such as CMC, can reduce the grammage and/or the amount of strengthening mixture.

Another considerable application for pulps produced according to the invention are soft

tissues, in which the bonded cellulose derivative will increase water retention.

The invention can also be used for producing modified fiber products that, on account of their good water retention, can be used in hygiene products, such as diapers.

5

According to the invention, the sorption can be even achieved essentially without separate retention chemicals, even though they can also be used. Preferably, an amount in excess of 50 % of the cellulose derivative in the solution will be bonded into the fibers.

- 10 In the following, the invention will be discussed in more detail using a detailed description of the invention and some working examples.

The following drawings graphically illustrate test results of pulps treated with CMC and, correspondingly paper sheets made from these pulps, in which

- 15 figure 1 illustrates the CMC content of fibers using different refining grades,  
figure 2 illustrates the results of water retention tests,  
figure 3 illustrates the filtration times of pulp,  
figure 4 illustrates the total retention of the pulp,  
figure 5 illustrates the opacity of the paper as a function of tensile index,  
20 figure 6 illustrates the air permeability of the paper as a function of tensile index,  
figure 7 illustrates the internal bond strength of the paper as a function of density.

- The invention is exemplified by using carboxymethyl cellulose and its sorption into cellulose pulp as an example. Even though CMC represents an especially preferred  
25 embodiment, it is to be noted, that the principles described in the invention can also be applied for other cellulose derivatives, such as methyl cellulose, hydroxyethyl cellulose and hydroxypropyl cellulose, that are similar in the respect of bonding. The properties, for example strength and/or water absorption, of cellulose fibers can be modified by means of these derivatives.

30

In the examples described below, the solution according to the invention is used for modifying the fibers of chemical pulp. In this context, chemical pulp means pulp that has been treated with cooking chemicals for delignifying the cellulose fibers. According to an

advantageous embodiment of the invention, the invention is applied to pulps produced with sulphate process and other alkaline processes. "Sulphate process" in this context means a cooking method in which the main cooking chemicals are sodium sulphide and sodium hydroxide. Extended cooking, in which a conventional sulphate process is continued until  
5 the kappa value of the pulp is below 20, can be mentioned as an example of other alkaline processes. Typically, these methods include oxygen treatment. The invention can as well be used for modifying the properties of pulps produced with acid cooking methods. Peroxo-alkane acid cooking can be mentioned as an example of acid cooking methods.

- 10 In addition to chemicals pulps, the present invention is suitable for modifying chemi-mechanical and mechanical pulps.

According to the invention, the cellulose derivative (described in the following as CMC) is introduced in liquid phase to contact the fibrous material, and the contact is continued until  
15 the cellulose derivative is bonded (sorbed) to the cellulose pulp so that it can not be washed off. The cellulose derivative can be added as solids directly to the pulp containing fibrous material, whereby the pulp is subjected to efficient dispersion to dissolve the CMC.

However, it is more efficient to perform contacting by first forming a water or alkaline solution from the CMC, with the solution being mixed with the pulp containing fibrous  
20 material. This kind of solution or suspension is homogenized in room temperature or elevated temperature ( $<100^{\circ}\text{C}$ ), insoluble material is separated either centrifugally or by filtration, and the clarified main solution is recovered and used for bonding.

At least 10 %, preferably at least 20 %, especially preferably at least 30 % and most  
25 preferably at least 50 % by weight of the cellulose derivative in the bonding solution, is dissolved in water or water phase in the alkaline conditions of the sorption.

When performing the invention, an essential portion of the CMC in alkaline or water solution is being subject to bonding so that at least 10 % by weight, preferably at least 30  
30 % by weight, especially preferably at least 40 % by weight and most preferably at least 50 % by weight (or even considerably more: 60 - 95 % by weight) of the CMC is bonded from the solution to the fibers.

During testing we noticed that sorption takes especially place, if the CMC is not too soluble in water in neutral conditions. Degree of substitution (DS) of conventional CMC grades is too high (typically 0.5 - 0.6) for achieving sufficient bonding. Therefore, the present invention utilizes CMC grades with a DS below 0,5. In this context, the degree of substitution means the amount of substituted hydroxyl groups per anhydro-glucose unit. In neutral conditions, the water solubility of these CMC grades is about 20 weight-% at the most, preferably about 10 weight-% at the most, most preferably about 0 - 5 weight-%.

According to an advantageous embodiment of the invention, the used material is CMC, which is water-soluble in mainly alkaline conditions. The degree of substitution of these derivatives is, for example, about 0.2 - 0.3, whereby CMC is bonded in alkaline conditions, typically in pH value 8 - 13, or in the area of 0.3 - < 0.5, whereby bonding can even be accomplished in neutral conditions. Generally, the advantageous degree of substitution for the invention can be defined as about 0.2 - 0.4. CMC used in the invention is completely water-soluble in alkaline conditions or the alkaline solution contains only a small amount of insoluble residues causing turbidity. Generally, at least 80 weight-%, preferably at least 90 weight-% and especially at least 95 weight-% of the CMC is soluble in alkaline conditions mentioned above.

The alkaline solubility of CMC makes it possible that CMC first can be dissolved in an alkaline solution, subsequent to which the ordinary bonding can take place in essentially neutral conditions at a pH value of about 6 - 12, preferably about 7 - 10.

Another important factor controlling the bonding of CMC is its molecular weight. If the molecular weight is high, the bonding only occurs on the outer surfaces of the fibers. This kind of modification allows enhancing of the strength properties of the fibers. CMC grades with smaller molecules can, on the other hand, penetrate the internal cells of the fiber wall, which also increases the amount of bonded CMC.

According to an advantageous embodiment of the invention CMC with a degree of polymerization (DP) of about 100 - 5000, especially preferably about 600 - 4000, is used. CMC having a low DP can be bonded into the fiber in greater quantities, which can have an advantageous effect on, for example, water absorption and degree of reservation of the

fiber.

Commercially available CMC grades can be used for carrying out the invention, the CMC's having a suitable degree of substitution and molar mass. When necessary, the properties of CMC can be modified in liquid phase prior to mixing it with the fibrous material in the pulp (i.e. fiber suspension). It is especially advantageous to disintegrate CMC for lowering its molar mass. In an advantageous embodiment of this option CMC is first dissolved or suspended into water or alkaline solution, subsequent to which material is added into the liquid phase for chemically or enzymatically fragmenting the anhydroglucose chain of the CMC for producing a CMC with a decreased molar mass. Examples of suitable materials include hydrogen peroxide and other radical producers. If necessary, the disintegration can be enhanced by using a catalyst.

According to an advantageous embodiment of the invention CMC is disintegrated to decrease the viscosity of its water or alkali solution. Most suitably the viscosity is decreased by at least 20 %, advantageously 50 - 90 %. Reducing the viscosity to one third produces a CMC product that bonds considerably stronger than untreated CMC.

For the bonding, the pH of the fiber suspension is set to the above-mentioned value of 6 - 13, preferably to 6 - 10. A suitable base or acid is used for setting the pH. Preferably, bicarbonate or carbonate of alkali metal or alkali metal hydroxide are used as bases. Mineral acid or an acid salt is used as the acid. Sulphuric acid and its acid salts, such as alum, are considered the most suitable salts, and sodium bicarbonate, sodium carbonate and sodium hydroxide are considered the most suitable bases.

The fiber suspension and cellulose derivative are mixed for at least 1 minute, preferably for at least 5 minutes, especially preferably for at least 10 minutes and most preferably for 20 minutes before drying (for example web forming). If a high degree of bonding is desired, mixing times of several hours, such as from 1 hour to 10 hours, are possible. Temperature is not a critical factor, in unpressurized conditions the temperature is typically 10 - 100 °C, preferably about 20 - 80 °C. The amount of the cellulose derivative is 0.1 - 5 % by weight of the cellulose fibers.

As both cellulose fibers and CMC are anionic, they repel each other, whereby it is easier to achieve bonding by adding some kation to the suspension. Typically, the sodium ion (or, correspondingly, the kation) content in the bonding conditions should be more than 0.01 M, preferably more than 0.01 M and especially preferably more than 0.1 M.

5

The cellulose fiber suspension used for bonding can contain other fiber materials and additives, such as fillers. Calcium carbonate can be mentioned as an example of fillers. Retention promoting materials, such as sodium acetate, can be mentioned as an example of additives. The dry material content of the pulp is about 0,1 - 10 %. The water phase of the  
10 pulp can consist of, for example, clear filtrate of the paper machine white water.

The CMC can be contacted with the cellulose fibers in any step prior to web forming. CMC can be bonded either at the pulp mill or at the paper mill. Both of these have alkaline (or essentially neutral) liquid/pulp flows, in which the bonding step can be arranged. For  
15 improving the strength properties, it is preferable to perform bonding only after beating. Further, the strength properties will be improved, if the pulp is not dried after bonding and before web forming.

In the pulp mill, the sorption can be effected in an alkaline bleaching stage, such as in  
20 oxygen (O) or peroxide (P) stage.

In the paper mill, the sorption of CMC is most suitably effected subsequent to beating of the pulp. The treated pulp is filtered and washed subsequent to sorption, before introducing the pulp to the paper machine. The filtrate and washing solutions are recirculated and, if  
25 necessary, fresh CMC feed is combined with them.

The bonding of CMC can be performed in connection with peroxide bleaching of mechanical pulps, for example in connection with manufacture of LWC papers. A typical alkali addition in the P stage is about 10 - 15 kg NaOH / t, i.e. about 0.3 mol / kg. The  
30 alkali can also be first used when sorpting CMC in the pulp used as strengthening pulp, and from there it can be further introduced to the P stage. If the bonding of CMC is performed in a consistency of 10 %, the available alkali can increase the pH value to 12. Having the filtrate circulate around the bonding stage, even higher pH values can be

attained. The alkaline filtrate used in the bonding stage can be introduced to P stage, where the CMC present in the filtrate can be sorbed on the surface of the mechanical mass, thereby increasing the bonding characteristics thereof.

- 5 The bonding of the cellulose derivative can be performed as a batch or semi-batch process or as a continuous process by first arranging the pulp retention time to be sufficiently long for the utilized process apparatus. A continuous process is considered advantageous.

10 The fiber pulp is formed into a web using a paper or a paperboard machine in a way known per se. Usually, the thickness of the web is 30 - 500 g/m<sup>2</sup>. Soft tissues can be mentioned as examples of especially advantageous paper products.

The fiber suspension can also be dried for producing an absorbent fiber material used in, for example, hygiene products, such as diapers.

15

The amount of cellulose derivative that can be washed away from a CMC treated fibrous raw material after alkali displacement and water washing is about 10 %, at the most, at a temperature of 25 °C and neutral pH conditions. CMC is not removed during beating, either. When utilizing the present invention, the strength properties can be considerably  
20 improved according to the molar mass of CMC. When compared with untreated paper, the same internal bond strength can be achieved while reducing the amount of pulp amount at least 10 %.

CMC, when sorbed according to the invention, will increase the characteristic bond  
25 strength of the fibers. This means that a certain strength level can be achieved with a lower bonding level. Low bonding level, on the other hand, leads to advantageous properties, such as high opacity (printing papers) or good air permeability (packing materials). High water retention can be achieved already with a low amount of large-molecule CMC as long as the pulp is beaten before sorption.

30

In the following, the present invention is discussed in more detail using the following non-limiting embodiment examples.



**Example 1****Sorption of carboxymethyl cellulose into pulp fiber**

CMC was sorbed into sulphate pulp, both unbeaten and PFI beaten with different  
5 revolutions. The utilized pulp was ECF bleached softwood sulphate pulp produced by  
Kaukaa, with dry solids content of 50 %. The cold disintegration of the pulp was  
performed according to the standard method SCAN-C 18:65. The pulp was beaten with a  
PFI beater equipped and calibrated according to the standard method SCAN-C 24:67, the  
10 numbers of revolutions used were 1000, 2000, 4000 and 7000. After the beating, the  
Schopper-Riegler value of the pulps were determined according to the standard method  
SCAN-C 19:65 and the Canadian Freeness value was determined according to the standard  
method SCAN-C 21:65. The results are presented in table 1.

**Table 1. SR and CF numbers for pulps beaten for different numbers of revolutions.**

15

	PFI beating (revolutions)	SR value	CF value
20	0	14.5	710
	1000	15	680
	2000	16	660
25	4000	20	550
	7000	36	310

Carboxymethyl cellulose (Nymcel ZSB-10, F1226) having a substitution level of 0.20 was  
30 sorbed into the above-mentioned pulps using a rotating 8 liter pulp digester. The  
temperature was elevated to 60 °C in 20 minutes, and the temperature was kept at this level  
for an hour. pH of the sorption solution was 12.5, and the consistency of pulp used for the  
sorptions was 5 % (50 g/l). In the beginning of the sorption the CMC content was 0.5 g/l (1  
% of fiber). After sorption, the pulp was cooled, filtered and washed, until its pH was 6.  
35 Reference pulps were produced in the same conditions, without the CMC addition, as the  
CMC treated pulps.

The amount of CMC sorbed into the fiber was analyzed by determining the amount of  
CMC present in the solution after sorption. The CMC content of the sorption solution was  
40 determined by means of a phenolsulphur acid test using a glucose standard line, and the  
amount of CMC present in the fibers was calculated on the basis of the CMC loss of the

solution. The results are shown in figure 1.

As the figure shows, about a half of the used CMC (about 0.5 % of fiber) was sorbed into the unbeaten fibers, and the CMC content of the fibers increased along with the beating  
5 level of the pulp, i.e. almost all of the CMC (about 1 % of fiber) was sorbed into the pulp beaten for 4000 revolutions.

### **Comparison example**

#### **Adding starch to the pulp**

10

A batch of starch-modified pulp was also produced for comparing the properties of CMC pulp. The used starch was kationic potato starch ether Raisamyl 135, with a substitution level of 0.035. The starch was introduced to the pulp as a 0.5 % solution, the pulp having a consistency of 3 %. The amount of starch was 0.5 % of the amount of fiber. Starch was  
15 introduced both to unbeaten pulp and pulp treated with PFI beating for 4000 revolutions.

### **Example 2**

#### **Testing the pulp**

## 20 Methods

### 1. SR and CF values of pulp

The Schopper-Riegler value was redetermined after treatments according to the standard  
25 method SCAN-C 19:65 and the Canadian Freeness value was determined according to the standard method SCAN-C 21:65.

### 2. Water retention of fiber

30 The water retention of the fiber was analyzed by means of WRV determinations according to the proposed standard method SCAN-C 102 XE (4nd proposal). WRV determinations were performed using a Jouan GR 4 22 centrifuge.

### 3. Drainage properties

The drainage time of the pulp was determined using a DDA apparatus (Dynamic Drainage Analyser) manufactured by AKRIBI Kemikonsulter Ab. The used sample volume was 750 ml, the consistency of the sample was 0,6 % for pulps beaten for both 1000 and 2000 revolutions; for pulps beaten for 4000 and 7000 revolutions the consistency of sample was 0,2 %. The used partial vacuum was 0.14 bar. The used wire was delivered by the manufacturer, M 0,150 T 0,112.

### 4. Total retention

The total retention was analysed using a DPCJ apparatus (Dynamic Paper Chemistry Jar). The sample volume was 500 ml, the consistency of the sample was 0.2 %, and the agitation speed was 1000 krpm. The wire used in total retention determination was a 75 mesh wire.

The results of the water retention testing are shown in figure 2, the drainage times of the pulp are shown in figure 3 and the total retention of the pulp is shown in figure 4.

As the appended figures illustrate, the water retention of CMC treated pulps increased considerably in proportion to the amount of beating prior to sorpting the CMC. The water retention of a CMC treated pulp beaten for 2000 revolutions was already double the retention of corresponding reference pulp. The results point to the conclusion that a CMC treated pulp beaten to a high SR value is extremely suitable for producing of, for example, soft tissues.

The drainage time given in figure 3 is the period of time from the start of the determination to the point when air begins to be sucked to the wire through the formed sheet. The air permeability of the formed wet sheet was measured 60 seconds after the drainage time.

Figure 3 illustrates that CMC treated pulps were slower to drain than the corresponding reference pulps while forming a denser sheet than the reference sheets. We wish to point out at this point that even though the CMC treated pulps were thus slower to drain than the reference pulps having same beating level, the drainage was considerably faster when the

tensile strength was equal.

Figure 4 illustrates that the sorption of CMC to the pulp fibers does not have substantial effect on the retention of the pulp, but the total retentions of both the CMC treated pulps and the reference pulps beaten to a certain level were highly similar. Nevertheless, when the tensile strength levels are equal, the retention of the CMC treated pulps was better than that of the reference pulps.

### Example 3

#### 10 Production of laboratory sheets

Laboratory sheets were produced from the pulp samples for testing the technical properties of paper. The laboratory sheets were produced without white water according to the standard method SCAN-C 26:76 with the exception of drum drying (2 h, 60 °C) and the wet pressing (490 kPa) preceding it.

The grammage, thickness and density of the paper were measured from the laboratory sheets according to the standard methods SCAN-P 6:75 and SCAN P 7:75. The results are presented in table 2.

**Table 2. Specifications describing the common properties of the paper**

Sample	PFI beating (revolutions)	Grammage (g/m <sup>2</sup> )	Thickness (μm)	Density (kg/m <sup>3</sup> )
25 REF	0	60.8	126	483
	1000	65.2	117	559
30	2000	65.1	107	606
	4000	62.6	96.6	648
35	7000	60.7	87.6	693
CMC	0	66.8	125	533
	1000	67.3	110	611
40	2000	64.7	101	639
	4000	64.8	98.6	657
45	7000	65.4	94.3	694
Raisamyl	0	62.9	128	492
	4000	67.6	97.7	691

As the table describes, the densities of sheets produced from unbeaten and only slightly beaten CMC treated pulps were considerably increased when compared with the corresponding reference pulps. In the sheets produced from more extensively beaten pulps (4000 and 7000 revolutions) the density increase caused by CMC sorption was not significant.

#### Example 4

#### Properties of laboratory sheets

##### 1. Optical properties

The optical properties of sheets produced according to example 3 (ISO lightness, opacity, light-scattering coefficient, light absorption coefficient) were determined using an Elrepho reflectometer equipped and calibrated according to the standard method SCAN-G 1:75. The measured light-scattering values were used for calculating the relative bonded area, RBA describing the bonding level. The results are presented in table 3.

**Table 3. Specifications describing the optical properties of the paper**

Sample	PFI beating (revolutions)	ISO lightness (%)	Opacity (%)	Light-scattering coefficient (m <sup>2</sup> /kg)	RBA (%)	Light absorption coefficient (m <sup>2</sup> /kg)
REF	0	86.1	72.3	32.7	13.4	0.129
	1000	85.5	70.5	27.4	27.4	0.141
	2000	84.5	66.8	23.6	37.5	0.132
	4000	83.7	62.6	20.6	45.4	0.140
	7000	82.3	58.3	17.5	53.6	0.156
CMC	0	86.2	71.8	29.0	23.2	0.121
	1000	84.9	68.5	24.2	35.9	0.141
	2000	83.7	64.5	20.9	44.6	0.155
	4000	82.6	61.4	18.2	51.8	0.164
	7000	81.8	57.4	15.6	58.7	0.145
Raisamyl	0	86.5	71.6	30.8	18.4	0.121
	4000	82.6	60.8	17.4	53.9	0.138

Thus, the lightness and opacity of the sheets produced from CMC treated pulps was higher than those of the reference sheets having the same tensile strength. This is also clearly

shown in the appended figure 5, in which opacity is shown as a function of tensile index.

## 2. Roughness and air permeability

- 5 The roughness and air permeability of the paper were determined with a Bendtsen apparatus calibrated according to the standard method SCAN-P 21:67. The apparatus was equipped with both an air permeability measuring sensor and a roughness measuring sensor. In figure 6, the air permeability describing the porosity of the paper is shown as a function of tensile index. The figure illustrates that the laboratory sheets produced from
- 10 CMC treated pulp having a certain tensile strength were considerably more porous than corresponding laboratory sheets produced from reference pulps.

## 3. Mechanical properties

- 15 The tensile strength, stretch at break and tensile breaking load were determined using an MTS 400M -stretching apparatus, the distance between the fastening points of the paper sheet was 50 mm and the rate of elongation was 12 mm/min.

20 **Table 4. Specifications describing the mechanical strength of the paper, tensile strength**

Sample	PFI beating (revolutions)	Stretch index (Nm/g)	Stretch at break (%)	Tensile breaking load (J/kg)	Tensile stiffness index (kNm/g)	Elasticity module (GPa)
25	REF	0	31.7	3.56	854	3.53
		1000	44.2	4.73	1487	3.87
30		2000	61.0	5.61	2297	4.32
		4000	73.5	5.97	2933	5.15
35		7000	86.7	5.81	3282	5.89
	CMC	0	38.4	4.54	1261	3.52
40		1000	72.7	6.19	2832	4.44
		2000	89.1	6.03	3382	5.50
45		4000	94.2	6.12	3597	5.72
		7000	105.1	6.02	3900	6.20
45	Raisamyl	0	36.9	4.45	1175	3.18
		4000	83.5	5.98	3271	4.75

As the table illustrates, the tensile strengths of the laboratory sheets produced from CMC treated pulps were clearly higher than those of corresponding reference tensile strengths. Further, the RBA parameter (relation of bonding fiber area) was higher in the CMC treated pulps than in the reference pulps. Thus, sorption of CMC into the fibers had increased the  
5 amount of fiber bonds on a certain pulp beating level.

The tensile strengths of the sheets produced from CMC treated pulp were also considerably higher on a given bonding level than the tensile strengths of reference sheets, i.e. sorption of CMC into the fiber obviously also increased the bonding strength. Further, the stretch at  
10 break and tensile breaking load of sheets produced from CMC treated pulps were higher than those of the sheets produced from reference pulps.

#### 4. Internal bond strength

15 The measurements of the internal bond strength were performed using an Internal Bond Tester meter. The pressure of the tape was 50 lbs/sq.in for unbeaten samples and the samples beaten for 1000 revolutions, 100 lbs/sq.in for samples beaten for 2000 revolutions, 150 lbs/sq.in for samples beaten for 4000 revolutions and 200 lbs/sq.in for samples beaten for 7000 revolutions. The results are presented in figure 7.

20

The internal bond strengths of sheets produced from CMC treated pulps were considerably higher than the internal bond strengths of sheets produced from corresponding reference pulps, which is most probably due to the increase in characteristic bond strength caused by the sorption of CMC.

**Claims:**

1. A method of producing a modified fiber product, according to which method
  - cellulosic raw material is formed into a fiber suspension,
  - 5    – components modifying the properties of fibers are added to the fiber suspension and
  - fiber material is dried,**characterized in that**
  - alkyl derivative of cellulose is mixed into the fiber suspension in alkaline
  - 10    conditions, the derivative being at least partly dissolved in water, and
  - the derivative is allowed to be bonded to the fibrous raw material prior to drying the fibrous material so that the bonded cellulose derivative can not be washed off with water.
- 15   2. A method according to claim 1, **characterized** in that a paper or paperboard web having good strength properties or good water retention is produced.
3. A method according to claim 1, **characterized** in that a cellulose product having good water retention is produced for use in hygiene products.
- 20   4. A method according to any of claims 1 - 3, **characterized** in that the used alkyl derivative of cellulose is carboxymethyl cellulose, carboxyethyl cellulose, methyl cellulose, ethyl cellulose or ether derivatives of any of these.
- 25   5. A method according to any of the previous claims, **characterized** in that the alkyl derivative of cellulose is allowed to be sorbed to the cellulose from the water phase so that at least 10 %, preferably 20 %, and especially preferably at least 30 % of the derivative contained by the water phase is allowed to be sorbed to the cellulose.
- 30   6. A method according to any of the previous claims, **characterized** in that the pH value of the pulp is more than 8, preferably more than 10.
7. A method according to any of the previous claims, **characterized** in that the pulp is



mixed with the cellulose derivative for at least 5 minutes, preferably at least 10 minutes and especially preferably for at least 20 minutes before drying.

8. A method according to any of claims 1 - 7, **characterized** in that the cellulose derivative  
5 to be sorbed is alkali soluble carboxymethyl cellulose (CMC), the DS of which being less than 0.5.

9. A method according to claim 8, **characterized** in that the polymerization level of the CMC is about 100 - 5000.

10

10. A method according to claim 8 or 9, **characterized** in that the DS of the CMC is 0.2 - 0.4.

11. A method according to any of claims 1 - 7, **characterized** in that the cellulose  
15 derivative to be sorbed is hydroxy-propyl-methyl cellulose (HPMC), hydroxy-ethyl-methyl cellulose (HEMC) and hydroxy-buthyl-methyl cellulose (HBMC).

12. A method according to any of the previous claims, **characterized** in that about 10 %, at the most, of the cellulose derivative can be washed off the treated fibrous raw material at a  
20 temperature of 25 °C and a neutral pH value.

13. A method according to any of the previous claims, **characterized** in that in comparison with untreated paper, the same internal bond strength is achieved while using at least 10 % less pulp.

25

14. A method according to any of the previous claims, **characterized** in that the cellulose derivative is contacted with the cellulose fibers in an alkaline flow of a pulp or paper mill.

15. A method according to claim 14, **characterized** in that the cellulose derivative is  
30 contacted with the cellulose fibers in an alkaline bleaching stage, such as an oxygen (O) or peroxide (P) stage.

16. A method according to claim 15, **characterized** in that the cellulose derivative is

contacted with the cellulose fibers in the peroxide bleaching of mechanical pulp.

17. A method according to claim 16, **characterized** in that the cellulose derivative is first contacted with chemical pulp, subsequent to which the pulp is drained and the filtrate is  
5 introduced to the peroxide bleaching of mechanical pulp.

18. A method according to claim 14, **characterized** in that the cellulose derivative is mixed with the cellulose fibers subsequent to the beating of fibers.

10 19. A method according to any of the previous claims, **characterized** in that the web forming is performed without an intermediate drying of pulp after sorption of the cellulose derivative.

20. A method according to any of the previous claims, **characterized** in that the amount of  
15 cellulose derivative is 0.1 to 5 % by weight of the cellulose fibers.

21. A modified fiber product, **characterized** in that it contains at least 0.1 % of CMC by (dry) weight of the fibers bonded to the fibers, the DP of the CMC being about 100 - 5000 and the DS about 0.1 - 0.4.

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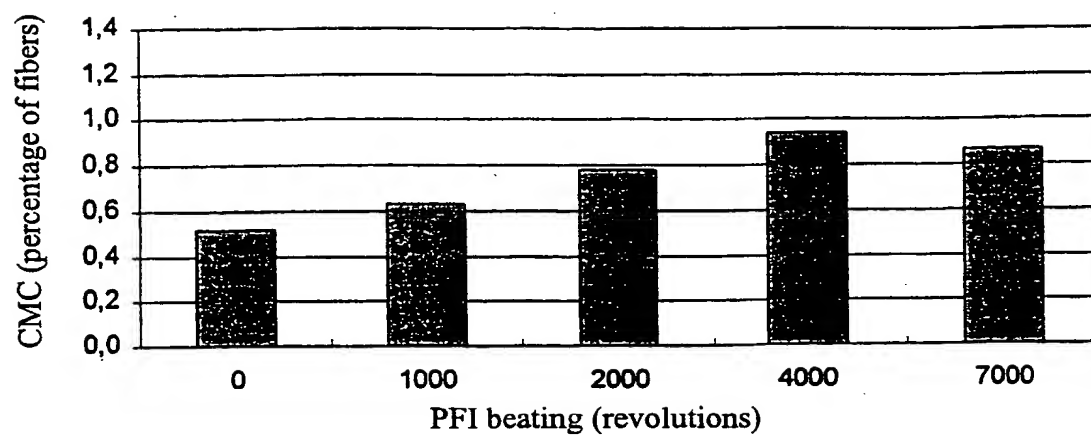


FIG. 1

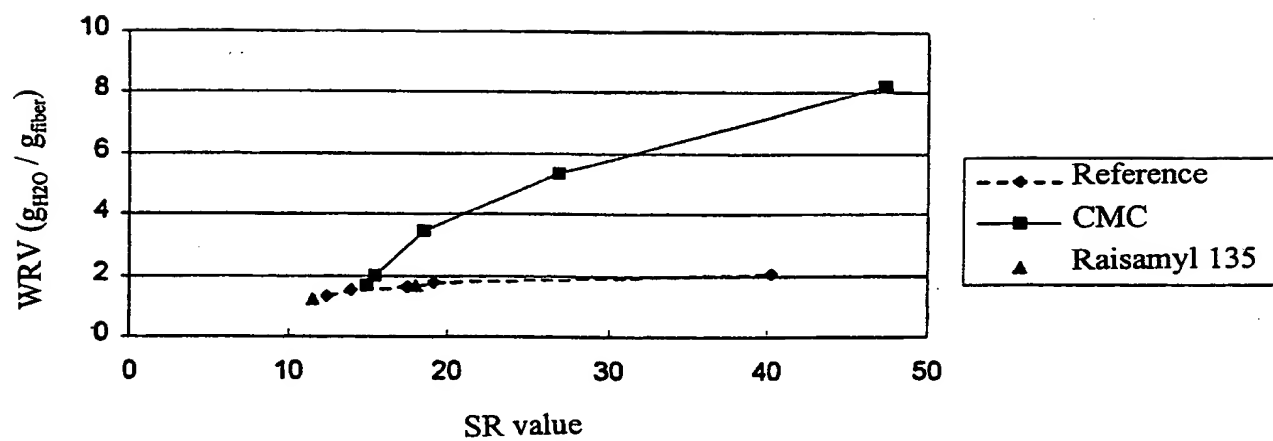


FIG. 2

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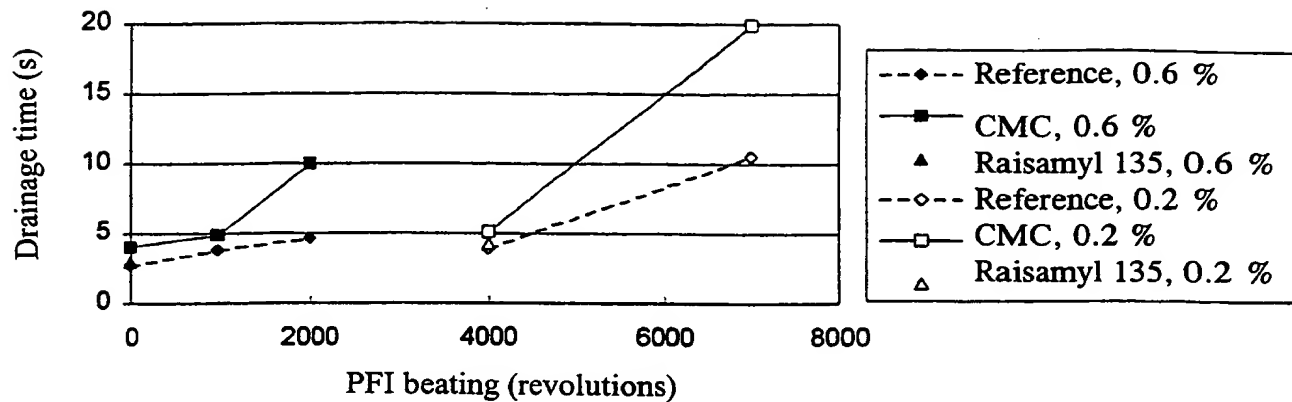


FIG. 3

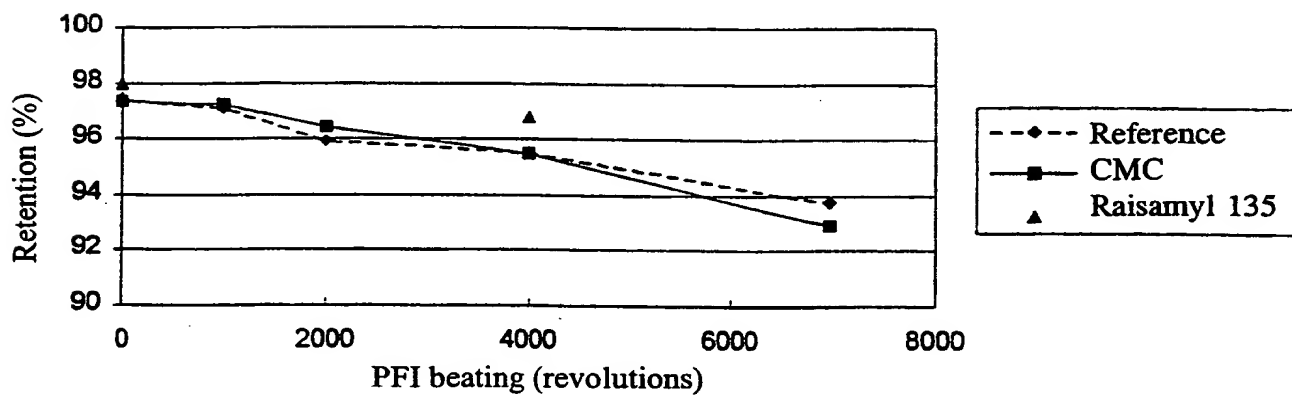


FIG. 4

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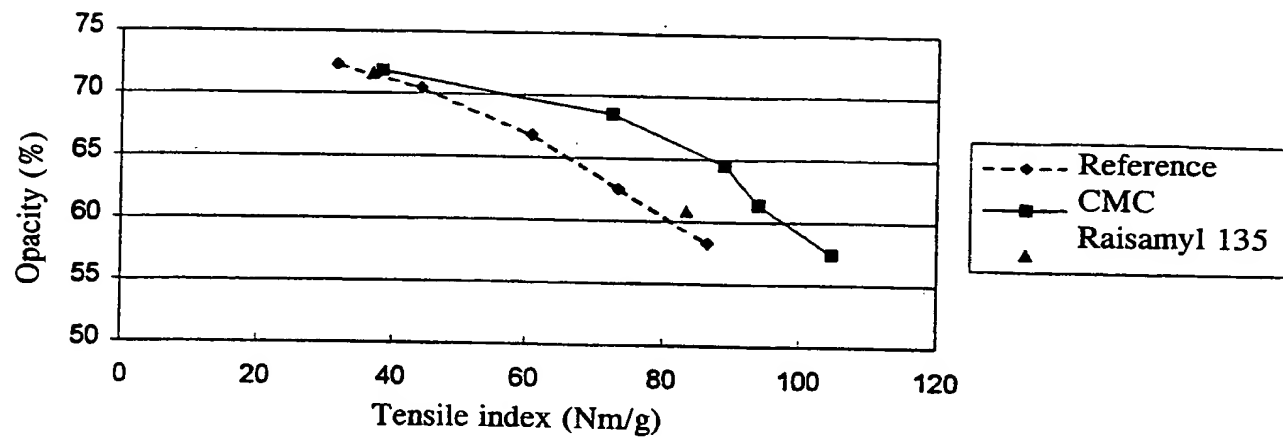


FIG. 5

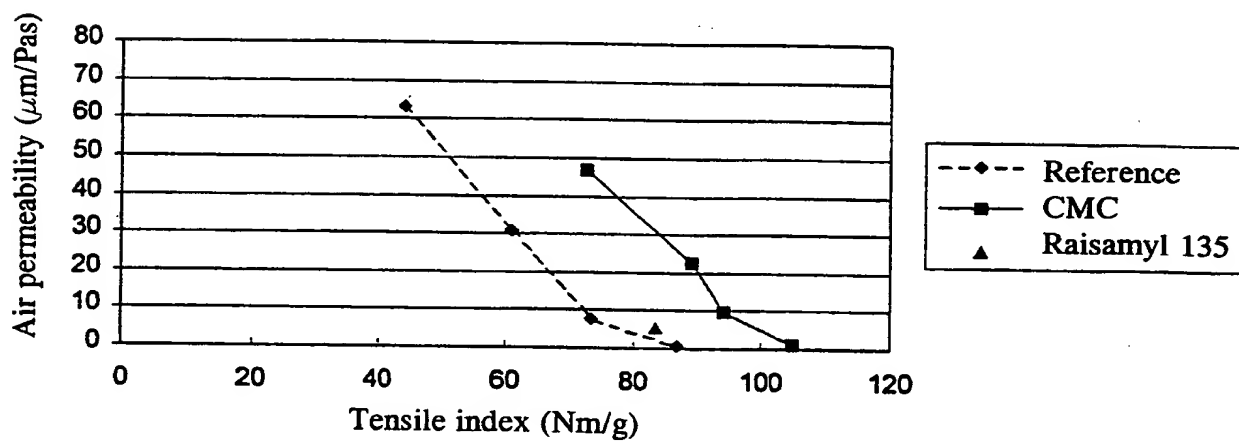


FIG. 6

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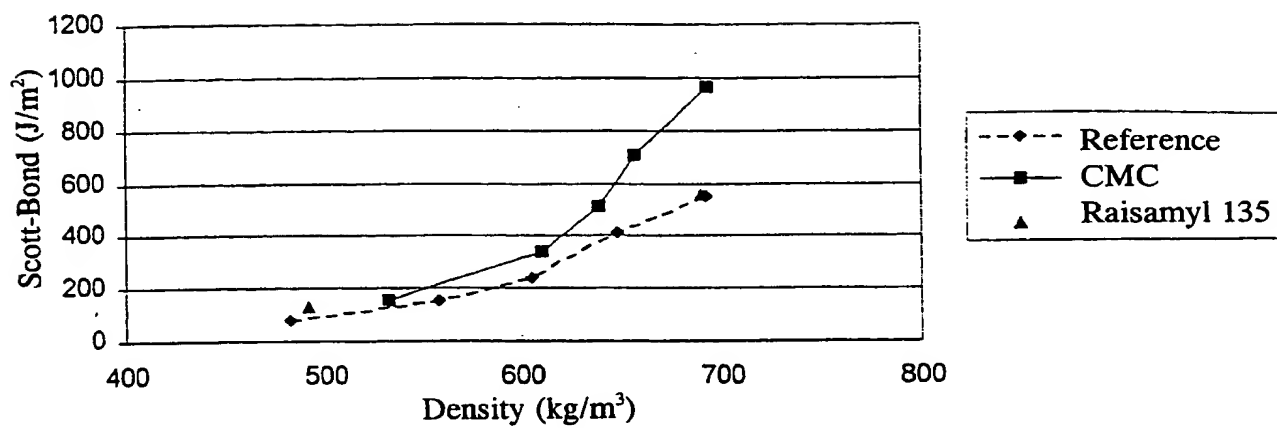


FIG. 7

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 99/00359

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>		
<b>IPC6: D21H 17/25</b> According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols)		
<b>IPC6: D21H</b>		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
<b>SE,DK,FI,NO classes as above</b>		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5354424 A (CHOKYUN RHA ET AL), 11 October 1994 (11.10.94), see claims 1-5; column 2, lines 28-31; column 5, lines 9-17; column 6, lines 56-64  --	1-21
X	File WPI, Derwent accession no. 98-603601, UNI-CHARM KK: "Hydrolytic sheet - includes base material sheet of water-dispersive fibre, and carboxyl methyl cellulose and/or its salt; and a liquid component"; & JP,A,10273892, 981013, DW9851  --	1
A	WO 9633310 A1 (THE PROCTER & GAMBLE COMPANY), 24 October 1996 (24.10.96), claim 1  --	1-21
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
24 August 1999		31 -08- 1999
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86		Authorized officer  Barbro Nilsson Telephone No. +46 8 782 25 00

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 99/00359

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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A	GB 1110004 A (BADISCHE ANILIN- & SODA-FABRIK AKTIENGESELLSCHAFT), 18 April 1968 (18.04.68), claims 1-3 --	1-21
A	GB 1111165 A (THE DEXTER CORPORATION), 24 April 1968 (24.04.68), claim 1 --	1-21
A	GB 1504128 A (IMPERIAL CHEMICAL INDUSTRIES LIMITED), 15 March 1978 (15.03.78), claim 1 -- -----	1-21



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